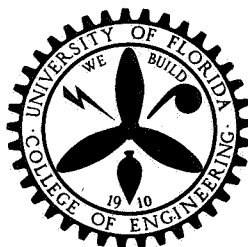


Quarterly Letter Report No. 8

March 15, 1968

SYNTHESIS OF ELASTOMERS FOR USE WITH
LIQUID FLUORINE



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ENGINEERING AND INDUSTRIAL EXPERIMENT STATION

College of Engineering

University of Florida

Gainesville

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SYNTHESIS OF ELASTOMERS FOR USE WITH
LIQUID FLUORINE

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to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT No. . NSR-10-005-047

Submitted by

Department of Chemical Engineering
Florida Engineering and Industrial Experiment Station

University of Florida
Gainesville, Florida

FOREWORD

This report has been prepared according to the provisions of Contract NSR-10-005-047, National Aeronautics and Space Administration, with the University of Florida and covers work performed during the period 1 December 1968 through 28 February 1969.

Personnel engaged in this work were Dr. Henry C. Brown, Principal Investigator, and Dr. A. R. Mukherjee.

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I. INTRODUCTION

The objective of this research is the synthesis of elastomeric polymers that will be resistant to the strong oxidizing effect of fluorine, oxygen difluoride, nitrogen tetroxide and similar agents. In addition, the material should be flexible at cryogenic temperatures.

During the present quarter, attempts have been made to synthesize trifluoromethyl hydroxamic acid and the corresponding isocyanate. This hydroxamic acid being rather unstable, attempts were made to stabilize it in the form of its copper salt. The reaction between trifluoromethyl isocyanate and ammonia was also studied further.

It was found that while synthesis of hydroxamic acids from the ethyl esters of perfluoroglutaric and perfluorosebacic acid was rather smooth, their conversion to the corresponding diisocyanates was quite difficult. Both the hydroxamic acids were produced in good yield and they are stable, high melting solids. Little or no isocyanate resulted on heating perfluoroglutaric hydroxamic acid with phosphorous pentoxide or polyphosphoric acid. In the case of perfluorosebacic hydroxamic acid, the yield was a mixture of isocyanate and acid or anhydride which could not so far be completely separated.

II. DISCUSSION

A. 1. Trifluoromethyl hydroxamic acid, its preparation and purification.

Trifluoromethyl hydroxamic acid is formed in good yield (80-90%) from the corresponding methyl ester and hydroxylamine, following the standard procedure. But among all the perfluoro monohydroxamic acids, it is the most hygroscopic in (transforms to a liquid on keeping in air) nature. It can almost completely be sublimed under vacuum at or above 50°, giving shining white drystals as sublimate. The crystals melt at 82-84° with some softening from 70°. The difference from the other monohydroxamic acids is pronounced in elemental analysis and infrared spectra; the elemental analysis of CF_3 hydroxamic acid shows a lower carbon and fluorine content and a higher hydrogen and nitrogen content, which can only be explained in terms of the presence of some free hydroxylamine in the system (elemental analysis of other hydroxamic acids are quite close to theory). Preparation of the hydroxamic acid from freshly distilled ester or reaction of the sublimed hydroxamic acid with excess of freshly distilled ester and subsequent purification by sublimation, etc., did not improve the analysis result. On addition of hydrochloric acid to the hydroxamic acid, some hydroxylamine hydrochloride separated (m.p. 151-153°C) as white crystals. The infra-red spectra of the trifluoromethyl hydroxamic acid showed some differences from the other hydroxamic

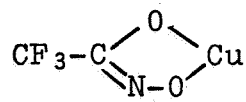
acids, peaks being found at 3-4 μ (somewhat broad), 5.8 μ , 6.0 μ , 6.2 μ , 6.45 μ , 6.7 μ , etc. Thus it might be concluded that trifluoromethyl hydroxamic acid is rather unstable in nature.

2. Stabilization of trifluoromethyl hydroxamic acid by Cu salt formation.

On addition of an aqueous solution of copper acetate to an aqueous solution of trifluoromethyl hydroxamic acid, a dark green, gelatinous copper salt separates and slowly settles overnight. On filtration, washing and drying, it gives dark green solid which is insoluble in organic solvents but quickly decomposes in acetic acid or ammonium hydroxide. It most probably decomposes at about 245°, as indicated by blowing out of the material from the melting point tube. It is very stable and nonhygroscopic; further purification is difficult as it is insoluble and cannot be sublimed. The infrared spectra shows peaks at 2.6-3.5 μ (weak, broad - OH?)(small hump, C=O?) 5.9 μ , 6.3 μ (Strong, C=N), 6.95 μ (strong CF₃), 8-9 μ (broad, C-F), 10.45 μ , 10.8 μ , 13.2 μ , etc.

The elemental analysis is quite close to theory, but does show a high value for carbon, low nitrogen and a trace of hydrogen. Most probably the sample contains a little copper acetate $\left[\text{Cu} (\text{CH}_3\text{COO})_2, \text{H}_2\text{O} \right]$, entrapped by co-precipitation, which cannot be removed by washing. This has been further confirmed by tracing the infrared spectra of a mixture of Cu(AC)₂, H₂O and the sample; the pattern of the spectra remained

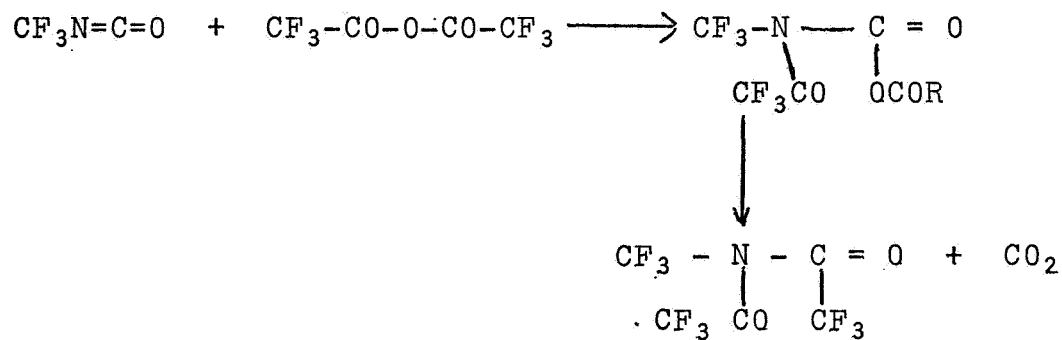
unchanged. The structure of the salt is evidently



3. Preparation of trifluoromethyl isocyanate from the corresponding hydroxamic acid.

Preparations of monoisocyanates from corresponding perfluoroalkyl hydroxamic acids, by heating them with P_2O_5 , have one problem in common - i.e. this reaction might get violent and go out of control. In the cases of C_2F_5 and C_3F_7 hydroxamic acids, the problem could be avoided by increasing the reaction temperature very slowly, thereby preventing any excessive heat generation. In case of CF_3 hydroxamic acid, however, this did not work; and, once the reaction starts, it proceeds with excessive heat generation and much of the product escapes. The problem was solved by mixing an inert material such as sand with the reaction mixture, which could take up most of the heat generated in the system and thus the reaction proceeded smoothly. The reaction products condensed in the trap and, coming out under vacuum at room temperature, were identified as CO_2 , CF_3NCO and $(\text{CF}_3\text{CO})_2$, respectively. Complete separation of CO_2 from CF_3NCO posed a problem due to close boiling points and some of CF_3NCO was lost in the process. The anhydride was most probably formed from the acid, generated by decomposition of hydroxamic acid. The formation of CO_2 can best

be explained by reaction between the anhydride and the isocyanate, as reported by Wurtz as early as 1854 [Ref: A. Wurtz, Ann. Chem. Phys., 42(3), 54(1854)]



Incidentally it may be mentioned that CO_2 was one of the reaction products in the preparation of C_2F_5 and C_3F_7 isocyanates also. The other reaction product must be higher boiling and might be in the residue left after distilling out isocyanates.

4. Reaction of trifluoromethyl isocyanate with ammonia.

The reaction product of pure CF_3NCO and excess NH_4 in ether is a white solid, almost insoluble in ether, acetone, tetrahydrofuran, etc., but partially soluble in water or methanol and completely soluble in caustic soda solution (as reported earlier). The reaction takes place with almost 50% increase in weight, thereby indicating addition of at least 3 mols of NH_3 to 1 mole of isocyanate. Part of this NH_3 is fixed as NH_4F , as indicated by presence of free F^- in the system. The F^- can, however, be removed from the system by

addition of $\text{Pb}(\text{NO}_3)_2$ to water soluble portion of the product, when PbF_2 separates (dil. acetic acid medium). Further separation of ingredients has not yet been possible.

B. 1. Preparation of perfluorosebaco hydroxamic acid.

Like the perfluoroglutaro hydroxamic acid, perfluorosebaco hydroxamic acid also has been prepared in good yield from the corresponding ethyl ester, following the standard procedure. The crude hydroxamic acid contains some NaCl and separation can be made by using acetone as solvent for the acid. Like the perfluoroglutaro hydroxamic acid, it does not crystallize out from solution nor does it sublime, even at 130°C under vacuum, and this further purification is not possible. The hydroxamic acid produced, however, has analysis results quite close to theory, (m.p. $193\text{--}195^\circ\text{C}$) and shows infrared peaks at 3.05μ (doublet, $-\text{NH}$, $-\text{OH}$) 3.45μ (hump), 5.9μ (strong, 3.15μ $\text{C}=\text{O}$), weak absorption at 6.5μ and 7.1μ , C-F absorption peaks at 8.25μ , 8.6μ , 8.75μ , etc. A sample heated at 155°C under vacuum gave some sticky sublimate, but infrared analysis showed some degradation.

2. Attempted synthesis of perfluoroalkyl diisocyanates.

Attempted synthesis of perfluoroglutaro diisocyanate by heating the hydroxamic acid with P_2O_5 resulted in some high boiling liquid collected under partial vacuum. The liquid product might contain some isocyanate as indicated by infrared

spectra. The yield was low and cyclization was expected at higher temperature. Better result can be expected, if the experiment is carried out under high vacuum with a lower reaction temperature. Another attempt was made with polyphosphoric acid as the dehydrating agent, but only some liquid product came out at high temperature under vacuum, which became solid and semi-solid at room temperature; this was apparently unreacted hydroxamic acid and probably some phosphoric acid. More favorable reaction conditions for this synthesis has not yet been found.

For synthesizing $(\text{CF}_2)_8(\text{NCO})_2$ from the corresponding hydroxamic acid, the hydroxamic acid was heated in the presence of P_2O_5 under vacuum and some liquid product was collected in the trap; the final product was mostly colorless liquid and some solid at room temperature. The liquid was decanted and distilled quite a number of times under N_2 atmosphere with different types of distillation arrangements; however, the boiling point gradually increased ($145-195^\circ$) with collection of distillate. The distillate showed infrared peaks at 4.4μ (strong $-\text{NCO}$) - two peaks of variable intensity at 5.3μ and 5.55μ (acid or anhydride), 6.8μ (strong $-\text{NCO}$), $8-9\mu$ (C-F), etc. Even distillation in a spinning band column gave the same result. The distillate was colorless hygroscopic liquid; elemental analysis showed carbon and hydrogen content close to theory but very high nitrogen content. The fraction collected

at 190-195° or at 38-39°/1-1.5mm did not show any I.R. peak at 5.3 , but the distillate was cloudy and some white solid separated out. Perhaps the solid sublimed under those conditions. This experiment is to be repeated.

III. EXPERIMENTAL

A. 1. Preparation of trifluoromethyl hydroxamic acid.

Method of preparation and purification was same as that described in Annual Interim Report, 1968, p 35-36.

Yield: 80-90%

Analysis

<u>Theory</u>		<u>Found.</u>	
		<u>A-53</u>	<u>A-53(R)</u>
18.6	%C	17.75	15.98
1.5	%H	2.59	2.14
10.9	%N	13.9	14.30
44.2	%F	39.9	-

* A-53 Sample prepared with long stored ester.

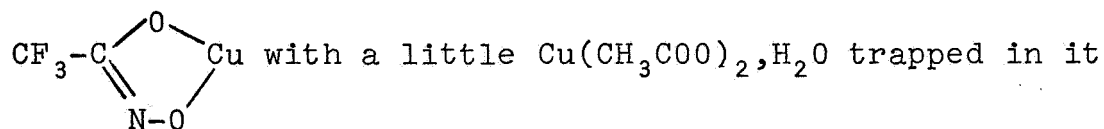
A-53(R) Sample prepared with freshly distilled ester.

Five grams of doubly sublimed CF_3CONHOH (A-53R) was dissolved in 10 ml CH_3OH and about 2-3 ml of freshly distilled $\text{CF}_3\text{COOCH}_3$ was added to it dropwise with stirring. The product left after vacuum drying was highly hygroscopic and showed the same type of infrared absorption spectra and other physical properties as the original product.

2. Preparation of the copper salt of trifluoromethyl hydroxamic acid

About 5 g of CF_3CONHOH (sublimed) was dissolved in 20 ml water. About 2 g of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was dissolved in 50 ml

of hot water and the solution was slowly added to the hydroxamic acid. An almost gelatinous dark green precipitate slowly settled overnight. It was filtered in a Gooch crucible and washed repeatedly with water, acetone, methyl alcohol and ether, then dried under vacuum at 100°. The sample was a dark, nonhygroscopic solid, with decomposition point at about 245°C. It is insoluble in any common solvent (sample A 279). A part of this sample was finely powdered and repeatedly washed with boiling water and dried under vacuum at 120°C (Sample A 279R). The analysis result and I.R. spectra of both the samples indicated the structure as



probably as co-precipitate.

Analysis Result

<u>Theory</u>		<u>Found.</u>	
		<u>A-279</u>	<u>A279R</u>
12.60	%C	12.94	12.8
0	%H	0.36	0.37
7.35	%N	6.45	6.56

3. Preparation of trifluoromethyl isocyanate.

Sublimed CF_3CONHOH (50 g), P_2O_5 (fresh, about 250 g) and sand (dried at about 220° and cooled under N_2 flow, about

1 kilogram.) were intimately mixed in a 2ℓ flask. The flask was attached to two dry-ice acetone-cooled traps and guard tubes for moisture and CO_2 and heated slowly. No product came out until the pot temperature reached about 200°C ; and the product then slowly evolved over 48 hrs. as pot temperature was slowly increased. Product consisted of some CO_2 , about 20 gms. of CF_3NCO and about 10 gms. of residual liquid having some $(\text{CF}_3\text{CO})_2\text{O}$ in it.

B. 1. Preparation of ethyl perfluorosebacate

Eighty-two grams (0.2 m) of crude $(\text{CF}_2)_8(\text{COOH})_2$ was mixed with 300 ml benzene, 80 ml absolute ethyl alcohol and 0.8 ml of conc. H_2SO_4 in a 2ℓ flask containing a stirring bar and reflux condenser with Drierite guard tube. The mixture was refluxed for 24 hrs. The azeotrope (b.p. 65°C and up) was taken out by using a distillation head. After 230 ml of distillate was collected and no further water was being formed, an additional 250 ml benzene and 80 ml absolute alcohol was added. The same procedure was repeated, then the last portions of solvents were taken out under vacuum. The ester $(\text{CF}_2)_8(\text{COOC}_2\text{H}_5)_2$, distilled at $125\text{--}127^\circ/2\text{--}3$ mm, yield 79 gms. of colorless liquid (86%). Some tar-like black material was left in the pot.

2. Preparation of $(\text{CF}_2)_8(\text{CONHOH})_2$

The method was the same as described in the Annual

Interim Report, 1968 (p 36).

Ingredients used:

$(\text{CF}_2)_8(\text{COOC}_2\text{H}_5)_2$ 0.1 m. 54.6 g
 $\text{NH}_2\text{OH} \cdot \text{HCl}$ 0.2 m. 14 g
 CH_3ONa 0.2 m, 10.8 g
 CH_3OH 500 Ml (Approx).

NaCl separated ... 7.5 g (Theor. 11.6 g). The crude product, a white, nonhygroscopic solid, about 55 g, contains some sodium chloride. It is almost insoluble in water, ether and ethylacetate; it is moderately soluble in tetrahydrofuran and mostly soluble in acetone. Extraction with tetrahydrofuran seems to be the best method of purification, NaCl being completely insoluble in that solvent. The sample did neither sublime at high temperature under vacuum nor crystallize out from solvents (Sample A 278).

m.p. : 193-195°C.

Result of analysis (Sample A 278).

<u>Theory or Range</u>		<u>Found</u>
23.0	%C	22.77
0.8	%H	0.97
5.4	%N	5.16

3. Attempted preparation of $(\text{CF}_2)_8(\text{NCO})_2$

Thirty gram of $(\text{CF}_2)_8(\text{CONHOH})_2$ was intimately mixed with about 150 g of P_2O_5 in a 500 ml flask; the flask was

connected to two dry-ice-cooled traps and guard tubes and heated. No product was evolved up to about 220°. Vacuum was applied and liquid product began to collect in first trap kept at room temperature. As pot temperature was increased, some of the product coming out solidified at room temperature. Finally about 8-10 ml liquid collected in first trap, along with some solid. The liquid was taken out and distilled under nitrogen atmosphere.

Distillate: B.P. 146-185°C, clear colorless liquid.

B.P. 185-195°C, cloudy liquid due to some suspended solid in it.

Distillation under vacuum, B.P. 38-40°C 1-1.5 mm, cloudy liquid distillate.

I.R. spectra: shows presence of some acid or anhydride in the isocyanate.

Analysis Result (Sample A-280, clear distillate).

<u>Theory</u>		<u>Found.</u>	
		In Duplicate	
24.8	%C	23.86,	23.59
0	%H	0.17,	0.19
5.8	%N	9.16,	9.40